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A TEST CASE OF KINETIC-THEORETICAL SCHEMES
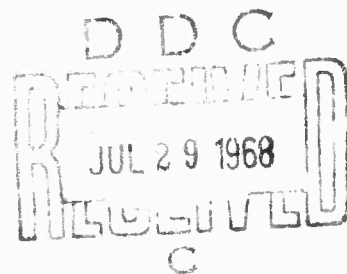
by

Toyoki Koga

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POLYTECHNIC INSTITUTE OF BROOKLYN

DEPARTMENT
of
AEROSPACE ENGINEERING
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DERIVATION OF THE BOLTZMANN EQUATION AS
A TEST CASE OF KINETIC-THEORETICAL SCHEMES *

by

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SUMMARY

The derivation of the Boltzmann equation from the Liouville equation can be a means of testing the feasibility of a kinetic-theroetical scheme, since the Boltzmann equation is known as empirically plausible. From this viewpoint , we investigate kinetic-theoretical schemes deriving the Boltzmann equation. We may derive the Boltzmann equation consistently by considering the Liouville equation to govern the distribution of a system in the phase space which is not symmetric in the microscopic sense. On the other hand, we cannot derive the equation consistently on the assumption of symmetry of the distribution; the Boltzmann collision integral is not compatible with the symmetry assumption.

I. INTRODUCTION

By examining usual procedures of the derivation of
the Boltzmann equation from the Liouville equation, we
find inconsistencies in the procedures. The main purposes
of this paper are: 1) to point out a common defect in the
functions of modern kinetic-theoretical schemes by
analyzing these inconsistencies and 2) to attempt eliminating
the inconsistencies; the attempt is the one to rationalize kinetic
theory itself.

The Boltzmann equation is a product of intuitive but
ingenious thoughts of Maxwell and Boltzmann.[1] In spite of
the intuitiveness involved in the original derivation, the
feasibility of the equation has been tested and confirmed
in many ways[‡] ; the equation is to be appreciated as a basic,
if empirical, law by itself. Therefore, as a means of proving
the feasibility of the Boltzmann equation itself, it is of no
significance to show a radical derivation of the equation from
the Liouville equation. On the contrary, it is more likely to
be a proof of the feasibility of a kinetic-theoretical scheme that
the scheme is able to derive consistently the Boltzmann equation
from the Liouville equation. In other words, the derivation of

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[†] It is well-known that the equation was proposed by Boltzmann
in 1872. We may see, however, that Maxwell's equations of trans-
fer proposed in 1866 would have stimulated Boltzmann to conceive
the equation. See The Scientific Papers of James Clark Maxwell
(Dover, N.Y.), Vol. II, p. 26.

[‡] S. Chapman and T.G. Cowling, The Mathematical Theory of Non-
Uniform Gases (Cambridge University Press, 1961), second edition.
For example, by assuming a proper law of interaction force between
molecules constituting a gas, we may calculate the viscosity co-
efficient and heat conduction of the gas according to the Boltzmann
equation.

the Boltzmann equation under certain conditions can be a
trial of the feasibility of kinetic-theoretical scheme. (Of
course, there may be a benefit that such a derivation shows
us more explicity conditions which limit the validity of the
Boltzmann equation.)

There have been attempts made by several authors to
derive the Boltzmann equation from the Liouville equation.[*]
In spite of their radical intention, however, the attempts do
not seem successful: For conceiving properly the Boltzmann
equation, it is necessary to make the concept of molar disorder
and that of molecular order as compatible. The compatibility
of these two conflicting concepts of states of particles in the
Boltzmann equation was made possible ingeniously by Boltzmann
and Maxwell by means of the Stosszahlansatz. On the other
hand, by a purely kinetic-theoretical approach, the compatibility
tends to be made possible only on the destruction of consistency
of the analyses. The common failure of known kinetic-theoretical
schemes deriving the Boltzmann equation is found at this point.
Then, changing our viewpoint, the very failure suggests to us that
there exists a basic and common defect in the structures of these
kinetic-theoretical schemes. That is the assumption of the

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[*]See section 4.

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microscopic symmetry of the distribution of a system in the phase space[*]. Based on this assumption, modern kinetic-theoretical schemes are not well-equipped with machinery by which it is possible to treat molar disorder and molecular order as compatible.

In section 2, basic concepts and definitions necessary for the dervation are introduced. It is stressed that the distribution of a system in the phase space is not symmetric in the microscopic sense. In section 3, it is shown that coarse-graining operations with respect to time and also with respect to similar particles are necessary for deriving the Boltzmann equation; the compatibility between molar disorder and molecular order is assured by the difference between the macroscopic and microscopic time scales. In comparison with the derivation given in section 3, we identify the common difficulty and its causes in known derivations by taking the Kirkwood-Ross derivation and the Bogoliubov derivation for examples in section 4. We also evaluate the derivation proposed by Grad which is rather anomalous.

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[*] The distribution is not symmetric in the microscopic sense. T. Koga, "Reply to Comments of P. Schram, Phys. Fluids, 6, 455 (1963); "A Kinetic Theoretical Investigation of a Fully Ionized Gas", Part I, PIBAL Report No. 863, January 1965.

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II. PREPARATORY DEFINITIONS AND TREATMENTS

The Liouville equation governing the evolution of
the distribution of a system consisting of N similar particles
(material points) is

$$\left(\frac{\partial}{\partial t} + \sum_{i=1}^{N} \frac{p_i}{m} \cdot \frac{\partial}{\partial r_i} + \sum_i \mathcal{F}_i \cdot \frac{\partial}{\partial p_i} \right) D^{(N)} = 0 \qquad (2.1)$$

with

$$\mathcal{F}_i = \sum_j \mathcal{F}_{ij} \, , \, \mathcal{F}_{ij} = -\mathcal{F}_{ji}, \, \mathcal{F}_{ii} = 0 \qquad (2.2)$$

Here $D^{(N)}$ is the distribution function of the system in the
phase space, t is time; m is the mass of a particle; p_i is
an independent variable representing a point in the momentum
space for particle i; r_i is an independent variable representing
a point in the position-vector space for particle i; $\mathcal{F}_i$ is
the total force exerted on particle i; $\mathcal{F}_{ij}$ is the force exerted
on particle i by particle j. It is assumed that there is no
external force exerted on the system. Since we are investigating
a single system, $D^{(N)}$ is to be given by

$$D^{(N)} = \sum_{i=1}^{N} \delta(X_i - X_i^*(t)) \qquad (2.3)$$

where X_i is a six-dimensional vector standing for p_i and r_i

$$X_i = p_i, \ r_i$$

and $X_i^*(t)$ constitutes a set of solutions of the equations of motion of the N particles. It is noted that $D^{(N)}$ is not symmetric with respect to the interchange of coordinates between any two particles*:

$$D^{(N)}(X_1, \ldots, X_i, \ldots, X_j, \ldots, X_N)$$

$$\neq D^{(N)}(X_1, \ldots, X_j, \ldots, X_i, \ldots, X_N) \qquad (2.4)$$

Distribution functions of subsystems are defined as follows:

$$F_i^{(1)}(X_i;t) = V \int D^{(N)} \prod_{j \neq i} dX_j \qquad (2.5)$$

where

$$dX_j = dp_{jx} \, dp_{jy} \, dp_{jz} \, dr_{jx} \, dr_{jy} \, dr_{jz}$$

and V is the volume of a domain of the configuration space in which the system is known to exist throughout the entire period of time of our investigation; the domain may be chosen arbitrarily as long as it is sufficiently large that the system or its part will not run off the domain. Once it is chosen, however, the domain

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See footnote on page 4.

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should not be changed during our investigation. Further we define

$$F_{ij}^{(2)}(X_i; X_j; t) = V^2 \quad D^{(N)} \underset{k \neq i, j}{\pi} dX_k, \quad \text{if } i \gtreqless j \qquad (2.6)$$

$$= 0 \qquad\qquad\qquad \text{if } i = j \qquad (2.6)'$$

and so forth. It is noted that the order of subscripts attached to $F^{(2)}$ is the same as the order of the same set of subscripts attached to the X's in $F^{(2)}$. This accordance of the orders means that there has been no interchange of coordinates among particles. According to the definition, it holds that

$$F_{ji}^{(2)}(X_j, X_i; t) = F_{ij}^{(2)}(X_i, X_j; t) \qquad (2.7)$$

and

$$F_{ji}^{(2)}(X_i, X_j; t) \neq F_{ij}^{(2)}(X_i, X_j; t) \qquad (2.7)'$$

in view of (2.4).

By integrating Eq. (2.1), term by term, with respect to the coordinates of all the particles except for particle i, we obtain*

$$(\frac{\partial}{\partial t} + \frac{P_i}{m} \cdot \frac{\partial}{\partial r_i}) \ F_i^{(1)}(X_i; t)$$

(continued on next page)

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*

Because of the finiteness of V and of the energy of the system, it holds that

$$\int \frac{\partial}{\partial p_k} D^{(N)} dp_k = 0, \int \frac{\partial}{\partial r_k} D^{(N)} dr_k = 0$$

Therefore

$$\int F_{ji} \cdot \frac{\partial}{\partial p_j} F^{(2)} dX_j = 0$$

This term is retained in equation (2.8) for the convenience of the further treatment of the equation.

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$$+ \frac{1}{V} \sum_{j=1}^{N} \int (\mathcal{F}_{ij} \cdot \frac{\partial}{\partial P_i} + \mathcal{F}_{ji} \cdot \frac{\partial}{\partial P_j}) F_{ij}^{(2)} (X_i, X_j; t) dX_j = 0$$

(2. 8)

If the integration is made with respect to all the particles except for particle i and particle, j, we obtain

$$(\frac{\partial}{\partial t} + \frac{P_i}{m} \cdot \frac{\partial}{\partial r_i} + \frac{P_j}{m} \cdot \frac{\partial}{\partial r_j} + \widehat{\mathcal{F}}_{ij} \cdot \frac{\partial}{\partial P_i} + \widehat{\mathcal{F}}_{ji} \cdot \frac{\partial}{\partial P_j}) F_{ij}^{(2)} (X_i, X_j; t)$$

$$+ \frac{1}{V} \sum_{k} \int (\mathcal{F}_{ik} \cdot \frac{\partial}{\partial P_i} + \widehat{\mathcal{F}}_{jk} \cdot \frac{\partial}{\partial P_j}) F_{ijk}^{(3)} (X_i, X_j, X_k; t) dX_k = 0$$

(2. 9)

We may increase the number of particles of exception so that the equations of evolution of $F^{(3)}$ and others are derived successively.

By making averages with respect to particles, we define

$$\overline{F^{(1)}(X_a; t)} \Delta X_a = \frac{1}{N} \sum_{i=1}^{N} \int_{X_a}^{X_a + \Delta X_a} F_i^{(1)} (X_i; t) dX_i$$

(2. 10)

$$\overline{F_{io}^{(2)}(X_i, X_b; t)} \wedge X_b = \frac{1}{N} \sum_{j} \int_{X_b}^{X_b + \Delta X_b} F_{ij}^{(2)} (X_i, X_j; t) dX_j$$

(2. 11)

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$$\overline{F_{oj}^{(2)}}(X_a, X_j; t) \, \Delta X_a = \frac{1}{N} \sum_i \int_{X_a}^{X_a + \Delta X_a} F_{ij}^{(2)}(X_i, X_j, t) \, dX_i$$

$$\overline{F^{(2)}}(X_a, X_b; t) \, \Delta X_a \Delta X_b \qquad\qquad (2.12)$$

$$= \frac{1}{N^2} \sum_i \sum_j \int_{X_a}^{X_a + \Delta X_a} \int_{X_b}^{X_b + \Delta X_b} F_{ij}^{(2)}(X_i, X_j; t) \, dX_i dX_j$$

$$(2.13)$$

Functions of X_i and/or X_j are discontinuous functions as shown
by (2.3), but functions of X_a and/or X_b may be continuous as
the number density of particles increases. In the above, it is
worthwhile to recall that X_i, X_j, etc. are independent variables.

Defined by

$$f(c, r; t) dr dp / m^3 = N \, F^{(1)}(p, r; t) dr dp \qquad (2.14)$$

$$c = p/m, \quad dr = dr_x dr_y dr_z, \quad \text{etc.}$$

f is the number density of the particles specified with velocity
c and position vector r at time t.

It is often assumed that f defined by (2.14) is the very
function which evolves according to the Boltzmann equation. We
note, however, that there is a difference between f and the function

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to be governed by the Boltzmann equation as is explained in
the following. The Boltzmann equation is postulated by

$$(\frac{\partial}{\partial t} + c \cdot \frac{\partial}{\partial r}) \, f'(c, r; t)$$

$$= \int_{0}^{\infty} [\, f'(c_1', r; t) \, f'(c', r; t) - f'(c, r; t)]$$

$$|c_1 - c| \, d\varphi \, h dh dc_1 \qquad\qquad (2.15)$$

According to the definition of the Boltzmann equation, c, c_1, c' and
c_1' must be velocities of particles only in free flight; therefore
f' should be defined so that f' gives the number density of such
particles only. Angle φ and length h are variables specifying
the geometrical relation of a collision between two particles which
begins with initial (asymptotic) velocities c and c_1 of the
two particles, as are illustrated in Fig. 2.1; c' and c_1' are the
final (asymptotic) velocities of the two particles after the collision.
In Eq. (2.15), c, c_1, and h are independent variables; in accordance
with the equations of motion of two particles, a collision may
begin either with c and c_1 or with c' and c_1' and ends, respectively,
either with c' and c_1'. By the Boltzmann equation, the evolution
of f' is due to the effects of many collisions accounted for in such a
manner that the effect of each collision is the integral of the

relevant differential effect over the entire phase of the collision. On the other hand, the evolution of $F_i^{(1)}$ according to Eq. (2.8) is due to the effects of collisions accounted for at given X_i which may be a state of particle i during a collision as well as during a free flight. See the schematic comparison given in Fig. 2.2. Therefore f defined by (2.14), which counts in not only the number density of particles in free flight but also that of particles during their collisions, is not the very distribution function to be governed by the Boltzmann equation. However, if the portion of a unit time during which a particle is in interaction with others is much smaller than the other portion during which the particle is in free flight, we may eliminate small and sudden fluctuations in f due to particles in collisions, by making an average of f over a time period from t to t + τ.

$$<f>_0 = \frac{1}{\tau} \int_0^\tau f(c, r(s); t + s) ds \qquad (2.16)$$

where

$$\frac{dr(s)}{ds} = c, \qquad r(0) = r$$

If τ and $r(\tau) - r$ are negligibly small in the macroscopic sense

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and yet large in the microscopic sense, $<f>_0$ defined above is equivalent to f in the macroscopic sense. In the microscopic sense, $<f>_0$, unlike f itself, is a smooth function of t presenting only the density of particles in free flight. Therefore it is more plausible to take $<f>_0$, instead of f, for the distribution function f' to be governed by the Boltzmann equation (2. 15) ,

$$f' = <f>_0 \qquad (2. 17)$$

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III. DERIVATION OF THE BOLTZMANN EQUATION

First, we assume that the significant interactions among particles are always binary. In other words, if $\mathcal{F}_{ij}$ is significant, then $\widetilde{\mathcal{F}}_{ik}$ and /or $\mathcal{F}_{jk}$ are negligible. According to this assumption, the integral term in Eq. (2.9) vanishes:

$$(\frac{\partial}{\partial t} + \frac{P_i}{m} \cdot \frac{\partial}{\partial r_i} + \frac{P_j}{m} \cdot \frac{\partial}{\partial r_j} + \mathcal{F}_{ij} \cdot \frac{\partial}{\partial p_i} + \widetilde{\mathcal{F}}_{ji} \cdot \frac{\partial}{\partial p_j}) \, F_{ij}^{(2)}(X_i, X_j; t)$$

$$= 0$$

$$(3.1)$$

Secondly, we assume that the scale τ_1 of gas dynamical processes in the system is much longer than the time scale τ_2 of inter-particle interaction:

$$\tau_1 >> \tau_2$$

During the time period from t to t +s, we consider fictitious trajectories of particle i which satisfy

$$\frac{dr_i(s)}{ds} = \frac{P_i}{m} , \quad r_i(s) = r_i + \Delta r_i(s)$$

$$(3.2)$$

$$\frac{dp_i}{ds} = 0 \qquad \text{(Trajectories 0)}$$

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with initial conditions

$$r_i(0) = r_i \qquad (3.3)$$

Here r_i and p_i are independent variables, but $r_i(s)$ is a function of time s.   These fictious trajectories are named trajectories 0.   Taking τ so that

$$\tau_1 \gg \tau \gg \tau_2 \qquad (3.4)$$

we make the average of each term of Eq. (2.8) along the trajectories 0 over s from 0 to τ.   On consideration of

$$\frac{\partial}{\partial t} F_i^{(1)}(p_i, r_i(s); t) = \frac{\partial}{\partial s} F_i^{(1)}(p_i, r_i(s); t + s)$$

$$\frac{p_i}{m} \cdot \frac{\partial}{\partial r_i} F_i^{(1)}(p_i, r_i(s); t + s) = \frac{p_i}{m} \cdot \frac{\partial}{\partial r_i(s)} F_i^{(1)}(p_i, r_i(s); t + s)$$

we may see that

$$\frac{1}{\tau} \int_0^\tau \left[\left(\frac{\partial}{\partial t} + \frac{p_i}{m} \frac{\partial}{\partial r_i} \right) F_i^{(1)}(X_i; t) \right]_{t \to t+s} ds$$

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$$= \frac{1}{\tau} \int_0^\tau \left(\frac{\partial}{\partial s} + \frac{P_i}{m} \cdot \frac{\partial}{\partial r_i(s)} \right) F_i^{(1)}(P_i, r_i(s); t+s) \, ds$$

$$= \left(\frac{\partial}{\partial t} + \frac{P_i}{m} \cdot \frac{\partial}{\partial r_i} \right) < F_i^{(1)}(X_i; t) >_0$$

$$(3.5)$$

where

$$< F_i^{(1)}(X_i; t)>_0 = \frac{1}{\tau} \int_0^\tau F_i^{(1)}(P_i, r_i(s); t+s) \, ds$$

$$(3.6)$$

By coarse-graining Eq. (2.8) in the above sense, we obtain

$$\left(\frac{\partial}{\partial t} + \frac{P_i}{m} \cdot \frac{\partial}{\partial r_i} \right) < F_i^{(1)}(X_i; t)> 0 + <J_i>_0 = 0$$

$$(3.7)$$

where

$$J_i = \frac{1}{V} \sum_{j=1}^N \int \left(\mathcal{F}_{ij} \cdot \frac{\partial}{\partial P_i} + \mathcal{F}_{ji} \cdot \frac{\partial}{\partial P_j} \right) F_{ij}^{(2)}(X_i, X_j;) dX_j$$

$$\left\langle J_i \right\rangle_0 = \frac{1}{\tau V} \int_0^\tau \sum_{j=1}^N \int \left[\left(\mathcal{F}_{ij} \cdot \frac{\partial}{\partial n_i} + \mathcal{F}_{ji} \frac{\partial}{\partial P_j} \right) F_{ij}^{(2)}(X_i, X_j; t) \right] dX_j \, ds$$
$$t \rightarrow t+s$$

$$(3.8)$$

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For deriving the Boltzmann collision integral from (3. 8),
we consider the following three points which are commonly
essential in statistical investigation:

1. In (3. 8), the summation with respect to j is made first
and then the result is averaged with respect to s. In order to
make the time average separately with respect to each of particles
j, it is necessary either to choose τ sufficiently short that particle
i interacts with particles j once, at most, during the time between
t and t + τ, or to assume that the interactions are very weak.
(Suppose that there are two strong collisions of particle i during
the period between t and t + τ. The effect of one collision when
it occurs first is different from the effect of the same collision
when it is assumed to occur second. Note that X_i is an independent
variable and is the same in the two cases, but $F_i^{(1)}$ in the first case
is different from $F_i^{(1)}$ in the second.) The necessity of the above
condition will be discussed again with respect to (3. 22).

2. Since we are observing $< F_i^{(1)}(X_i;t)>_0$, i = 1, 2, 3, ...,
it is impossible and also unnecessary for us to know the precise
time when the precise state with which a particular particle j
begins to interact significantly with particle i. Thus we may

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set the same assumption as the Stosszahlansatz by Boltzmann
with respect to the state with which particle j begins to interact
significantly with particle i during the time between t and t + τ:
Particle j is one of the particles which are located near particle
i at time t, and among which $D^{(N)}$ may be assumed to be symmetric.
If we take Δr_b for the domain of the configuration space in which
such particles j exist, definition 2.11 leads to;

$$\langle J_i \rangle_0 = \frac{N-1}{V} \int_0^\tau \iint_{\Delta r_b} \left[\widehat{\mathscr{F}}_{ib} \cdot \frac{\partial}{\partial P_i} F_{io}^{(2)}(X_i, X_b; t) \right]_{t \to t+s} dX_b \, ds$$

(3.8) '

Note that the domain of the integration with respect to dr_b is
limited by Δr_b in accordance with the definition of $F_{io}^{(2)}$ which
is continuous unlike $F_{ij}^{(2)}$. Further, on coarse-graining with
respect to i in accordance with (2.13), we have

$$\langle \overline{J} \rangle_0 = \frac{N-1}{V} \int_0^\tau \iint_{\Delta r_b} \left[\widehat{\mathscr{F}}_{ab} \cdot \frac{\partial}{\partial P_a} \overline{F^{(2)}(X_a, X_b; t)} \right]_{t \to t+s} dX_b \, ds$$

(3.8)''

On consideration of the above, Eq. (3.7) yields

$$\left(\frac{\partial}{\partial t} + \frac{P_a}{m} \frac{\partial}{\partial r_a} \right) \overline{\langle F^{(1)}(X_a; t) \rangle} + \langle \overline{J} \rangle_0 = 0$$

(3.7)'

3. The result of the coarse-graining must be independent of τ. Otherwise, the result has no definite physical meaning. The situation depends on the distribution of particles in Δr_b and τ. If the distribution is uniform, the result is perfect. As the density of a gas becomes more rarefied and the distribution of particles in Δr_b and τ becomes more non-uniform, the result tends to depend on τ. Then the possibility of kinetic theory diminishes.

Instead of $\langle J_i \rangle_0$, we may make $\langle J_i \rangle_I$ by coarse-graining J_i over time from t to $t + \tau$ along trajectories I which satisfy

$$
\frac{dr_i(s)}{ds} = \frac{p_i(s)}{m} \ , \quad \frac{dp_i(s)}{ds} = \widehat{\mathcal{F}}_{ij}(s)
$$

$$
\left. \frac{dr_j(s)}{ds} = \frac{p_j}{m} \ , \quad \frac{dp_j(s)}{ds} = \widehat{\mathcal{F}}_{ji}(s) \right\} \qquad (3.9)
$$

(Trajectories I)

with initial conditions

$$
r_i(0) = r_i, \quad p_i(0) = p_i
$$

$$
r_j(0) = r_j, \quad p_j(0) = p_j \qquad (3.10)
$$

Thus we obtain

$$
\langle J_i \rangle_I = \frac{1}{\tau V} \int_0^{\tau} \sum_j \int_{X_j} \left(-\frac{dp_i(s)}{ds} \cdot \frac{\partial}{\partial p_i(s)} + \frac{dp_j(s)}{ds} \cdot \frac{\partial}{\partial p_j(s)} \right)
$$

$$
F_{ij}^{(2)}(X_i(s), X_j(s); t+s) dX_j ds \qquad (3.11)
$$

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Equations (3. 9) constitute the characteristic equations of Eq. (3. 1) if $\partial/\partial t$ is replaced with ∂/∂ and t with t + s. Therefore, by integrating Eq. (3. 1) along trajectories I given by (3. 9), we obtain

$$\int \frac{d}{ds} F_{ij}^{(2)} (X_i(s), \ X_j(s); \ t + s) \ ds$$

$$= \Big| \ F_{ij}^{(2)} (X_i(s), \ X_j(s); \ t + s)\Big|_o^\tau \ = 0 \qquad (3.\,12)$$

where

$$\frac{d}{ds} = \frac{\partial}{\partial s} + \frac{dr_i(s)}{ds} \cdot \frac{\partial}{\partial r_i(s)} + \frac{dr_j(s)}{ds} \cdot \frac{\partial}{\partial r_j(s)}$$

$$+ \frac{dp_i(s)}{ds} \cdot \frac{\partial}{\partial p_i(s)} + \frac{dp_j(s)}{ds} \cdot \frac{\partial}{\partial p_j(s)}$$

By making the average of $<J_i>_I$ with respect to particles in the same way as is shown by (2. 13), we obtain

$$\overline{<J>}_I = \frac{N}{\tau V} \int_o^\tau \int_{\Delta r_b} \Big(\frac{dp_a(s)}{ds} \cdot \frac{\partial}{\partial p_a(s)} + \frac{dp_b(s)}{ds} \cdot \frac{\partial}{\partial p_b(s)} \Big)$$

$$\overline{F^{(2)}(X_a(s), X_b(s), \ t + s)} \ dX_b \ ds$$

$$(3.\,14)$$

where Δr_b is of the same implication as stated with respect to (3.8)'. On definition of $\left[\dfrac{d}{ds}\right]_{ab}$ by

$$\left[\frac{d}{ds}\right]_{ab} = \frac{\partial}{\partial s} + \frac{P_a(s)}{m} \cdot \frac{\partial}{\partial r_a(s)} + \frac{P_b(s)}{m} \cdot \frac{\partial}{\partial r_b(s)}$$

$$+ \mathcal{F}_{ab}(s) \cdot \frac{\partial}{\partial p_a(s)} + \widehat{\mathcal{F}}_{ba}(s) \cdot \frac{\partial}{\partial p_b(s)}$$

$$(3.15)$$

relation (3.14) yields

$$\overline{\langle J \rangle}_1 = \frac{N}{TV} \int_0^T \int_{\Delta r_b} \left(\left[\frac{d}{ds}\right]_{ab} - \frac{\partial}{\partial s} - \frac{P_a(s)}{m} \cdot \frac{\partial}{\partial r_a(s)} \right.$$

$$\left. - \frac{P_b(s)}{m} \cdot \frac{\partial}{\partial r_b(s)} \right) \overline{F^{(2)}(X_a(s), X_b(s); t + s)}$$

$$dX_b \, ds$$

$$(3.16)$$

Unlike (3.12), $\left[\dfrac{d}{ds}\right]_{ab} \overline{F^{(2)}}$ in the above integrand does not vanish. The reason is that

$$\overline{\mathcal{F}_{ab} \cdot \frac{\partial}{\partial p_a} F^{(2)}(X_a X_b; t)} \neq \overline{\widehat{\mathcal{F}}_{ab} \cdot \frac{\partial}{\partial p_a} F^{(2)}(X_a X_b; t)}$$

etc.

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ΔX_a and ΔX_b considered in (2.13) cover domains of the configuration space which are larger than the domain of the force field induced by a single particle; hence only a few of all the particles among two groups of particles, one group in states between X_a and $X_a + \angle X_a$ and the other in states between X_b and $X_b + \Delta X_b$, are really participating in binary collisions of the mode specified by (3.13); many of them are in collisions of different modes and/or in free flight. Hence we may write for (3.16)

$$\overline{\langle J \rangle}_I = \frac{N}{TV} \int_{\Delta r_b} [\ F^{(2)}(X_a(\tau), X_b(\tau); t + \tau)$$

$$- F^{(2)}(X_a, X_b; t)]\, dX_b$$

$$- \frac{N}{TV} \int_0^\tau \int_{\Delta r_b} \left(\frac{\partial}{\partial s} + \frac{dr_a(s)}{ds} \cdot \frac{\partial}{\partial r_a(s)} + \frac{dr_b(s)}{ds} \cdot \frac{\partial}{\partial r_b(s)} \right)$$

$$F^{(2)}(X_a(s), X_b(s); t + s)\, dX_b\, ds$$

$$(3.17)$$

It will be show that the first integral in the above yields the Boltzmann collision integral while the second integral is insignificant

if the number density particle is as low as usual.

Particles in state X_b may interact with particles in state X_a during the period of time between t and t + τ only if r_b at time t is chosen in the domain of the configuration space between r'_b and r''_b respectively defined by

$$(r'_b - r_a) \cdot (p_b - p_a) = 0$$

$$\frac{(r''_b - r_a) \cdot (p_b - p_a)}{|p_b - p_a|^2/m} = - \tau \qquad (3.18)$$

as is illustrated in Fig. 3.1. Hence, by presenting r_b with a cylindrical coordinate system with the origin at r_a and the altitude in the direction of $p_b - p_a$, we have

$$\Delta r_b = \int dr_b = - \tau \frac{|p_b - p_a|}{m} \int d\varphi h dh$$

$$(3.19)$$

Here φ stands for the direction angle and h the radius in the plane of zero altitude. We also assume that, before and after a collision between two particles, the correlation between the two particles is weak so that

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$$\overline{F^{(2)}(X_a, X_b;t)} = \overline{F^{(1)}(X_a;t)} \ \ \overline{F^{(1)}(X_b;t)}$$

$$\overline{F^{(2)}(X_a(\tau), X_b(\tau);t+\tau)} = \overline{F^{(1)}(X_a(\tau); t+\tau)} \ \ \overline{F^{(1)}(X_b(\tau); t+\tau)}$$

(3.20)

On consideration of (3.19), the second member in the right-hand side of (3.17) is of the order of

$$\frac{N}{\tau V} \int (\tau \frac{\partial}{\partial t} + \frac{\tau p_a}{m} \cdot \frac{\partial}{\partial r_a} + \frac{\tau p_b}{m} \cdot \frac{\partial}{\partial r_b}) \overline{F^{(2)}(X_a, X_b;t)}$$

$$dp_b \ \tau \ \frac{|p_b - p_a|}{m} \ d\varphi \ h \ dh$$

$$= \frac{N \Delta r_b}{V} (\frac{\partial}{\partial t} + \frac{p_a}{m} \cdot \frac{\partial}{\partial r_a}) \overline{F^{(1)}(X_a;t)}$$

(3.21)

where Δr_b is given by (3.19) and is the volume of the configuration-space domain in which we find at t such particles as to interact with particles of state X_a in the future between t and $t + \tau$. It is reasonable[*], therefore, to assume that

$$0[\int d\varphi \ hdh] = \sigma = 5 \times 10^{-16} \ cm^3$$

where σ^2 is the order of cross section or σ is the maximum distance between two particles within which their interaction is significant

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[*]The assumption is reasonable only for neutral molecules. See for example, J.H. Jeans, The Dynamical Theory of Gases (Dover, N.Y.), fourth edition. p. 281.

and that

$$(N/V)^{-1/3} \ll 0[\tau(p_b - p_a)/m] \ll \text{mean free path length}^* = \frac{1}{2^{1/2} \pi c^2 N/V}$$

By choosing τ as in the above, we have

$$\sigma^3 \left(\frac{N}{V}\right)^{2/3} \ll \frac{N \Delta r_b}{V} \ll \frac{1}{2^{1/2} \pi} \doteq 0.2 \qquad (3.22)$$

If $N/V = 10^{21}$, then $\sigma^2 (N/V)^{2/3} = 5 \times 10^{-2}$. Under this condition, it appears barely possible to choose τ so that (3.22) is satisfied. If $N/V = 10^{24}$, then $\sigma^2 (N/V)^{2/3} = 5$, and (3.22) does not hold regardless of τ. It is noted that condition $N \Delta r_b/V \ll 1$ is the very condition that τ is short so that particle i interacts with other particles once at most during the time period between t and $t + \tau$. Note the statements which follow (3.8). Under condition (3.22), the term given by (3.21) is negligibly small as compared with the first two terms of Eq.(3.7). Thus, with the help of (3.19) and (3.20), Eq.(3.17) yields

$$\overline{\langle J \rangle}_I = -\frac{N}{V} \int \left[\overline{F^{(1)}(p_a(\tau), r_a(\tau); t+)} \; \overline{F^{(1)}(p_b(\tau), r_b(\tau); t+)} \right.$$
$$\left. - \overline{F^{(1)}(p_a, r_a; t)} \; \overline{F^{(1)}(p_b, r_b; t)} \right]$$
$$\frac{|p_b - p_a|}{m} \, d\varphi \; h \, dh \, d \, p_b$$

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*See J.H. Jeans, The Dynamical Theory of Gases

If we consider that τ, $r_a(\tau)-r_a$ and $r_b(\tau)-r_b$ are of microscopic scales and hence

$$\overline{F^{(1)}(p_a, r_a(\tau); t+\tau)} = \overline{\left\langle F^{(1)}(p_a, r_a; t)\right\rangle_0}$$

etc.

in the time scale of τ_1, we finally have

$$\overline{\langle J\rangle}_I = -\frac{N}{V}\int\left[\overline{\left\langle F^{(1)}(p_a(\tau), r_a; t)\right\rangle_0}\ \overline{\left\langle F^{(1)}(p_b(\tau), r_a; t)\right\rangle_0}\right.$$

$$\left. - \overline{\left\langle F^{(1)}(p_a, r_a; t)\right\rangle_0}\ \overline{\left\langle F^{(1)}(p_b, r_a; t)\right\rangle_0}\right]$$

$$\frac{|p_b - p_a|}{m}\, d\varphi\, h\, dh\, d p_b$$

$$(3.25)$$

Since $\left\langle J_i\right\rangle_0$ and $\left\langle J_i\right\rangle_I$ are made by averaging respectively along trajectories 0 and trajectories I, these two averages are not mutually equivalent. In the following, however, it will be shown that

$$\overline{\left\langle J(X_a; t)\right\rangle}_0 = \overline{\left\langle J(X_a; t)\right\rangle}_I \qquad (3.26)$$

after their being coarse-grained with respect to particles in the same way as is shown by (2.13): J_i is a function of X_i and t, and exists along a line named J_i in the $X_i t$-space as is shown schematically in A of Fig.3.2. By the assumption of binary collision, line J_i coincides with

one of the trajectories I. Since we are dealing with a
single system, J_i vanishes unless particle i is in
interaction with particle j so that $\widehat{\pi}_{ij}$ is significant.
Almost straight lines in the same illustration are
trajectories O. In B of Fig.3.2, J_i, $\left\langle J_i \right\rangle_O$ and $\left\langle J_i \right\rangle_I$
are shown at time t. J_i appears as presented by
δ-function; $\left\langle J_i \right\rangle_I$ also appears as if δ-function,
since J_i exists only on one of the trajectories I.
On the other hand, $\left\langle J_i \right\rangle_O$ made by averaging J_i
along trajectories O is shown as if an error function.
Obviously

$$\left\langle J_i \right\rangle_O \neq \left\langle J_i \right\rangle_I \qquad (3.27)$$

It is obvious, however, that

$$\int \left\langle J_i(X_i;t) \right\rangle_O dX_i = \int \left\langle J_i(X_i;t) \right\rangle_I dX_i \qquad (3.28)$$

This is because both are the same total intensity of
J_i from t to $t + \tau$ divided by τ. If the number of
particles which exist in states between X_a and $X_a + \Delta X_a$
is sufficiently large, we may assume

$$\overline{\left\langle J(X_a;t) \right\rangle_O} = \overline{\left\langle J(X_a;t) \right\rangle_I} \qquad (3.26)$$

where, of course,

$$\overline{\left\langle J(X_a;t) \right\rangle_O} = \frac{1}{N\Delta X_a} \sum_i \int_{X_a}^{X_a + \Delta X_a} \left\langle J_i(X_i;t) \right\rangle_O dX_i \qquad (3.29)$$

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$$\left\langle J(X_a;t) \right\rangle_I = \frac{1}{N \Delta X_a} \sum_i \int_{X_a}^{X_a + \Delta X_a} \left\langle J_i(X_i;t) \right\rangle_I dX_i \quad (3.30)$$

Needless to say, condition (3.28) is compatible with (3.26). According to the above, Eq.(3.7)' yields

$$\left(\frac{\partial}{\partial t} + \frac{a}{m} \cdot \frac{\partial}{\partial r_a} \right) \overline{\left\langle F^{(1)}(X_a;t) \right\rangle_0} + \overline{\left\langle J \right\rangle_I} = 0 \quad (3.31)$$

In order to reduce Eq.(3.31) to Eq.(2.15), it is necessary to replace $\overline{\left\langle F^{(1)} \right\rangle_0}$ with f' in accordance with (2.14) and (2.16):

$$f'(c,r;t) = N m^3 \overline{\left\langle F^{(1)}(p,r;t) \right\rangle_0} \quad (3.32)$$

$$c = p/m \quad (3.33)$$

It may be a trivial matter that we take off subscript a, replace subscript b with 1, and write mc' and mc'_1 respectively for $p_a(\zeta)$ and $p_b(\zeta)$ for completing the reduction.

Finally, the essential points in the above derivation are summarized as follows:

1. We may take some other class of trajectories in place of trajectories 0, as long as they are equivalent

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in time scale $\overline{\zeta}_1$.

2. Also, trajectories I may be replaced with trajectories II, etc. , if these classes are equivalent in time scale $\overline{\zeta}_2$.

3. X_i is an independent variable, and $F_i^{(1)}(X_i;t)$ is a discontinuous function to be presented by δ-function. But $\overline{F^{(1)}}(X_a;t)$ is a continuous function, if N/V and ΔX_a are sufficiently large. The situation is similar with respect to $F_{ij}^{(2)}(X_i,X_j;t)$, etc.

4. Although

$$\frac{d}{ds} F_{ij}^{(2)}(X_i(s),X_j(s);t+s) = 0$$

in (3.12), yet

$$\left[\frac{d}{ds}\right]_{ab} \cdot \overline{F^{(2)}(X_a(s),X_b(s);t+s)} \neq 0$$

in (3.15).

5. The domain of integration $\int dr_b$ considered in (3.19) is finite in the direction of $p_b - p_a$. This is necessary, after replacing $F_{ij}^{(2)}(X_i,X_j;t)$ with $\overline{F^{(2)}}(X_a,X_b;t)$, for taking into account the fact that a particle with its finite velocity is localized in a narrow domain of the configuration space during a short

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period of time τ. Note that $F_{ij}^{(2)}(X_i, X_j; t)$ is discontinuously localized by itself, but that

$$\overline{F^{(2)}(X_a, X_b; t)}$$ is a continuous function. If $D^{(N)}$ were symmetric in the microscopic sense, the above limitation of the integration with respect to db_b would not be justified. Then the value of the collision integral would always be indefinitely large.

IV. DIFFICULTIES IN USUAL DERIVATIONS

There have been different derivations published by several authors. As typical examples, the derivations by Kirkwood and Ross, by Bogoliubov, and by Grad are investigated in the following. Because of the assumption of symmetry of $D^{(N)}$ considered in the microscopic sense, these derivations involve common difficulties.

4.1. Derivation by Kirkwood and Ross *

1. Being coarse-grained with respect to time, Eq.(2.8) yields

$$(\frac{\partial}{\partial t} + \frac{p_i}{m} \cdot \frac{\partial}{\partial r_i}) \langle F_i^{(1)}(X_i;t) \rangle_K$$
$$+ \frac{1}{V} \sum_{j=1}^{N} \int_0^{\tau} (\widehat{\mathcal{F}}_{ij} \cdot \frac{\partial}{\partial p_i} + \widehat{\mathcal{F}}_{ji} \cdot \frac{\partial}{\partial p_j}) F_{ij}^{(2)}(X_i, X_j; t+s) dX_j ds$$

$$(4.1)$$

where

$$\langle F_i^{(1)}(X_i;t) \rangle_K = \frac{1}{\tau} \int_0^{\tau} F_i^{(1)}(X_i;t+s) ds \qquad (4.2)$$

By assuming that the distribution is symmetric, we may replace

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*J. Kirkwood and J. Ross, The Statistical Mechanical Basis of the Boltzmann Equation, in Proceedings of the International Symposium in Statistical Mechanics, Brussels, 1965, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958.

$$F_i^{(1)}(X_1;t) \quad \text{with } F^{(1)}(X_1;t)$$

$$F_{ij}^{(2)}(X_i,X_j;t) \quad \text{with } F^{(2)}(X_1,X_2;t) \tag{4.3}$$

$$\overline{\sum_j} \quad \text{with } N$$

The next procedure is to define $K^{(2)}$ by

$$F^{(2)}(X_1,X_2;t+s) = \int K^{(2)}(X_1,X_2/X_1',X_2';s) \, F^{(2)}(X_1',X'_2;t)dX_1' \, dX_2'$$

$$\tag{4.4}$$

Since $K^{(2)}$ is given explicitly by

$$K^{(2)}(X_1,X_2/X_1',X_2';s) = \delta(X_1-X_1'-\Delta X_1(s)) \; \delta(X_2-X_2'-\Delta X_2(s))$$

$$\tag{4.5}$$

it is easily shown that

$$F^{(2)}(X_1,X_2;t+s) = F^{(2)}(X_1-\Delta X_1(s),X_2-\Delta X_2(s);t)$$

$$\tag{4.6}$$

According to Kirkwood and Ross, $\Delta X_1(s)$, standing for $\Delta p_1(s)$ and $\Delta r_1(s)$, and $\Delta X_2(s)$, standing for $\Delta p_2(s)$ and $\Delta r_2(s)$, are the changes in momenta and space coordinates of particle 1 and particle 2 determined by solving the equations of motion of the two particles in accordance with the assumption of

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binary collision:

$$\frac{d\,\Delta r_1(s)}{d\,s} = \frac{p_1 + \Delta p_1(s)}{m}$$

$$\frac{d\,\Delta p_1(s)}{d\,s} = \widehat{\mathcal{F}}_{12}(s) \tag{4.7}$$

and

similar equations for particle 2.

Under this circumstance, they claim that $F^{(2)}$ given by (4.6) is a solution of Eq.(3.1) where $\partial/\partial t$ is replaced with $\partial/\partial s$:

$$(\frac{\partial}{\partial s} + \frac{p_1}{m}\cdot\frac{\partial}{\partial r_1} + \frac{p_2}{m}\cdot\frac{\partial}{\partial r_2} + \widehat{\mathcal{F}}_{12}\cdot\frac{\partial}{\partial p_1} + \widehat{\mathcal{F}}_{21}\cdot\frac{\partial}{\partial p_2})F^{(2)} = 0 \tag{4.8}$$

Here s, p_1, p_2, r_1 and r_2 are to be independent variables. It is obvious, however, that $F^{(2)}$ given by (4.6) under condition (4.7) does not satisfy Eq.(4.8). Instead, it is obvious that $F^{(2)}$ satisfies Eq.(4.8), if $\Delta X_1(s)$ and $\Delta X_2(s)$ are solutions of

$$\frac{d\,\Delta r_1(s)}{d\,s} = \frac{p_1}{m} \,,\quad \frac{d\,\Delta p_1(s)}{ds} = \widehat{\mathcal{F}}_{12} \tag{4.9}$$

etc.

in place of (4.7). Note that p_1, p_2, r_1 and r_2 are independent of s in (4.9), and hence the equations are

not the equations of motion of the two particles. Only
when $\Delta X_1(s)$ and $\Delta X_2(s)$ are extremely small, Eqs.(4.9)
coincide with Eqs.(4.7). It is noted that the particular
solution of Eq.(4.8) integrated along trajectories determined
by Eqs.(4.7) is considered in (3.12).

2. Although $\Delta X_1(s)$ and $\Delta X_2(s)$ satisfying Eqs.(4.9)
are not the proper trajectories of the two particles in
interaction, such as expected to be by the authors, yet
$F^{(2)}$ given by (4.6) is a correct solution of Eq.(4.8)
under condition (4.9). Therefore, if the succeeding treatment
is proper, it may lead to a correct result. By substituting
$F^{(2)}$ given by (4.6) in the collision integral of (4.1),
however, we will meet a great difficulty in the following
treatment: Since X_1 and X_2 are independent variables, the
domain of the integration with respect to dr_2 is to be the
entire configuration space; $\widetilde{\mathscr{F}}_{12}$ and/or $\mathscr{F}_{21}$ are functions
of r_1 and r_2 , and are completely independent of $\Delta r_1(s)$ and

$\Delta r_2(s)$ by (4.9). Therefore, $\Delta r_1(\tau) - \Delta r_2(\tau)$ is not a
factor which affects the magnitude of $\mathscr{F}_{12}$. Even when
$\Delta r_1(\tau) - \Delta r_2(\tau)$ is extremely large, yet $\widehat{\mathscr{F}}_{12}$ may not
vanish if $r_1 - r_2$ is small, and vice versa. Hence,

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there is no reason for limiting the domain of integration
with respect to dr_2 in the direction of $p_2 - p_1$ by
$\zeta|p_2-p_1|/m$ that is a function of $\bar{\zeta}$.

3.   The difficulty mentioned in the above seems to
have stemmed from the authors' belief that the X's and
t must be always independent variables. This belief is
a rational consequence of their assumption that $D^{(N)}$
given in (2.1) is always symmetric with respect to the
interchange of coordinates between two similar particles.
Indeed, according to the assumption, it is pointless to
say that an individual particle moves along a continuous
trajectory; there is no such individual particle as
distinguishable from the others by its continuous trajectory.
In spite of the technical difficulty mentioned thus far,
it appears that the authors' approach is at least persistent
according to their belief that $D^{(N)}$ is symmetric, but the
situation is not necessary so: Against the authors'
expectation, $F^{(2)}(X_1- \Delta X_1(s), X_2 -\Delta X_2(s);t)$ given by (4.6)
is no more symmetric as is shown below. Suppose that we consider
$F^{(2)}$ at $X_1 = \Delta X_1(s)$ and $X_2 = \Delta X_2(s)$. Then, according to
the symmetry assumption, it must hold that

$$F^{(2)}(0,0;t) = F^{(2)}(\Delta X_2(s)-\Delta X_1(s), \Delta X_1(s)-\Delta X_2(s);t)$$

Since $\Delta X_2(s) - \Delta X_1(s)$ may increase as s increases,
the above equation implies that $F^{(2)}(X_1,X_2;t)$ is uniform
along a line given by $X_1 = -X_2$. If we displace the origin
of the coordinate system by keeping the axes as parallel to

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those before the displacement, we may realize that
$F^{(2)}$ is uniform (invariant) over the enitire phase space.
This obvious paradox is caused by the attempt to represent
a microscopic collision in terms of $F^{(2)}$ which is assumed
to be symmetric.

4. Microscopic collisions are conceivable only when
we begin a theory by taking $D^{(N)}$ of a single system as given by
(2.3) which is not symmetric. By taking $X_i = X_i^{\bullet}(s)$,
we are observing $D^{(N)}$ along the trajectory of particle i.
It is worthwhile to note that there are various solutions
of the partial differential equation (4.8), according
to our choice of functions of s to be assigned to p_1, p_2,
r_1, and r_2;

$$p_1 = p_1^{\bullet}(s), \quad r_1 = r_1^{\bullet}(s)$$
$$p_2 = p_2^{\bullet}(s), \quad r_2 = r_2^{\bullet}(s)$$
$$(4.10)$$

In the special case where these functions given in the
above satisfy the characteristic equations of Eq.(4.8)
which are the very equations of motion given by (3.9),
$F^{(2)}$ is invariant with respect to s. Otherwise, $F^{(2)}$
is not invariant.

In view of the above investigation, it appears that Kirkwood and Ross believed the symmetry of $D^{(N)}$ in the microscopic sense. (Another evidence of their belief is found in one[*] of Kirkwood's previous papers also.) This belief, in spite of their reasonable approach of coarse-graining with respect to time, seems to have jeopardized their derivation. In general, the same difficulty as is found in the derivation by Kirkwood and Ross is pointed out commonly in derivations beginning with the symmetry assumption of $D^{(N)}$.

4.2. Derivation by Bogoliubov[†]

The derivation by Bogoliubov is similar to the derivation by Kirkwood and Ross. Bogoliubov defined "streaming operator" which is of the same implication as that of $K^{(2)}$ given by (4.5). Therefore the difficulty seen in Bogoliubov's derivation is of the same nature as that of Kirkwood and Ross.

4.3. Derivation by Grad[‡]

The derivation by Grad is anomolous in the sense that the derivation is consistent in spite of the symmetry of $D^{(N)}$ assumed in the microscopic sense. This paradoxical situation is explained in the following. Grad defined "truncated distribution functions", e.g., $F_1^\sigma(X_1)$

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[*] J. Kirkwood, J. Chem. Phys. 14, 180(1946). Particularly the paragraph beginning in pg. 181 and ending in the next page is of interest from the present viewpoint. For a system to be investigated, he chooses one at random among those systems constituting a canonical ensemble. As a result, $D^{(N)}$ of the system is statistical from the beginning of his theory.

[†] N. N. Bogoliubov, Problems of a Dynamical Theory in Statistical Physics (1946), translated by E. G. Gora, in Studies in Statistical Mechanics, edited by J. de Boer and G. E. Uhlenbeck (North-Holland Publishing Co. 1962) Vol. I.

[‡] H. Grad, Principles of the Kinetic Theory of Gases, in Handbuch der Physik edited by S. Flugge (Springer-Verlag, Berlin 1958), Vol. XII pp. 205-295.

is the expectation of finding no molecule within

a distance σ of molecule 1, granting that molecule

1 is in state X_1. It is also assumed that the sphere of

radius σ limits the domain of influence of molecule 1.

Grad derives the equation of evolution of $F_1^{\sigma}(X_1)$ from

the Liouville equation, instead of the equation of

evolution of $F^{(1)}(X_1)$. This is equivalent to considering

the distribution function of molecules as in states of

free flight in the same way as is intended by the Boltzmann

equation [*]. Also by assuming the existence of the sphere

of influence, the further treatment appears as if a treatment

of collisions among elastic spherical bodies of diameter σ,

instead of collisions by means of force fields. Therefore

the spatial domain of the collision integral with respect

to a field particle is always the space outside the sphere

of influence of particle 1. In this way, Grad could

avoid the cause of the common difficulty, that is, the

consideration of trajectories of particles during their

collisions. In order to complete the derivation by

giving the equation obtained above the same implication

as that of the Boltzmann equation, however, it is necessary

to assume the existence of "molecular order" in the behavior

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[*] $F_1^{\sigma}(X_1)$ is equivalent to

$$\frac{1}{\tau} \int_0^{\tau} F^{(1)}(X_1; t+s)\, ds$$

if collisions are rare.

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of two particles within the distance σ. This
assumption is not compatible with the postul tion
that the symmetry of $D^{(N)}$ and hence the Bogoliubov-
Born-Green-Kirkwood-Yvon hierarchy are valid in
the microscoric sense. This condition is out of
the scope of Grad's theory. Grad's scheme is
ingeneous in the sense that it has separated itself
from the treatment of collision mechanism which is
not compatible with the symmetry assumption of $D^{(N)}$.

V. CONCLUSION

1. The feasibility of the Boltzmann equation
for neutral molecules has been tested and confirmed
by experiments.

2. The Boltzmann collision integral is derivable
from the Liouville equation only by considering that
the distribution function $D^{(N)}$ of a system is not
symmetric in the microscopic sense.

3. The microscopic symmetry of $D^{(N)}$, by which
a particle is indistinguishable from the others, is not
compatible with the Boltzmann collision integral where
a particle is distinguishable during its collision by

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its continuous and ordered trajectory.

4. By accepting the Boltzmann equation as feasible, we must admit that kinetic theory is to begin with $D^{(N)}$ which is not symmetric.
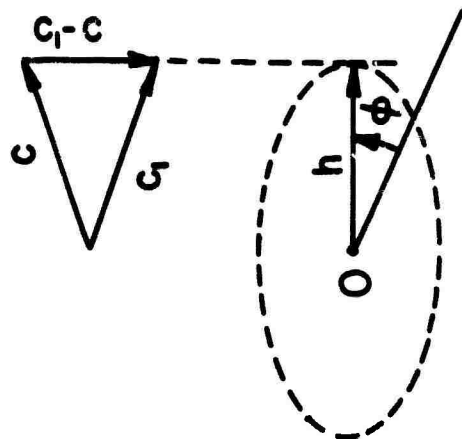
Fig. 2.1. Immediately before a collision between two particles, the particle with velocity c is at 0 and the particle with velocity c_1 is at 1. $c_1 - c$ is the relative velocity. Projected on the plane which passes 0 and is perpendicular to $c_1 - c$, the vector 0-1 is of length h and of direction ψ.
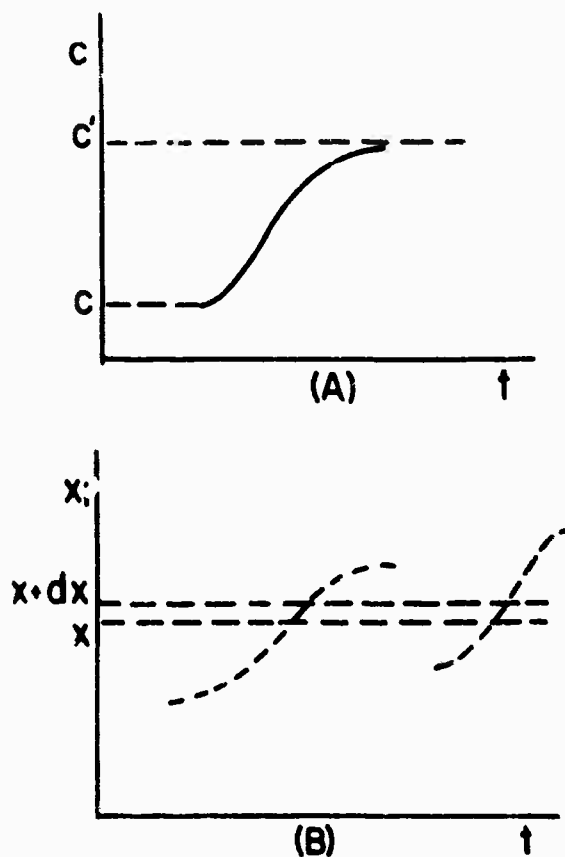
Fig. 2.2. In the Boltzmann equation, the effect of a
collision is an integral over the entire phase of the collision as is shown
in A. On the other hand, the effect of a collision in Eq. (2.8) is accounted
for only at X_i between X and X+dX as is shown in B. Reduction of the
Boltzmann equation from Eq. (2.8) is made possible by coarse-graining
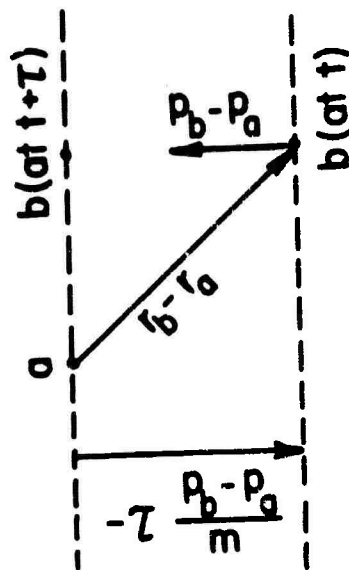Eq. (2.8) with respect to particles and time.

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Fig. 3.1. Particle a in state (r_a, p_a) and particle b in state (r_b, p_b) at time t will be at the shortest distance at $t + \tau$, if

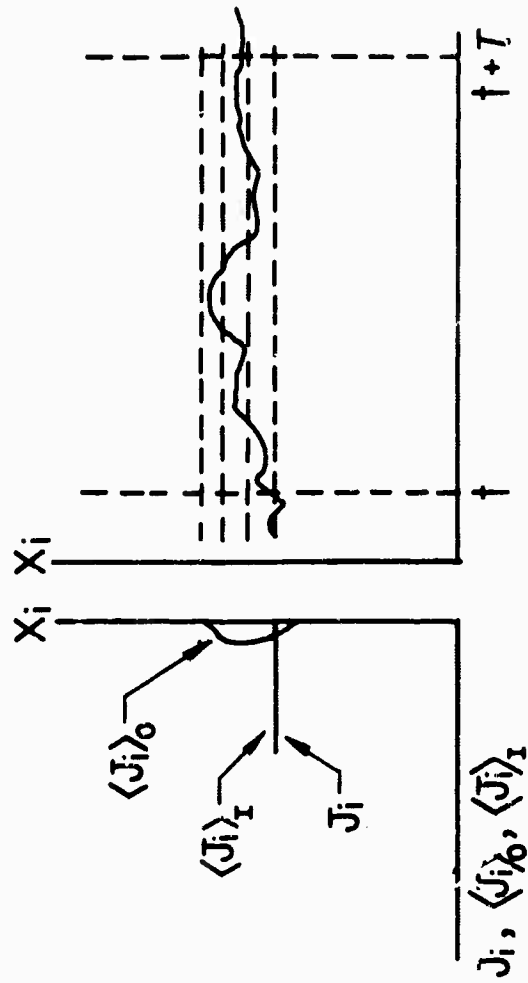$$-\tau \frac{|p_b - p_a|}{m} = \frac{(r_b - r_a) \cdot (p_b - p_a)}{|p_b - p_a|}$$

Fig. 3.2. J_i and $J_{i \ 1}$ appear as if they are δ-functions.
But $J_{i \ 0}$ is similar to an error function.

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13. ABSTRACT

The derivation of the Boltzmann equation from the Liouville equation can be a means of testing the feasibility of a kinetic-theoretical scheme, since the Boltzmann equation is known as empirically plausible. From this viewpoint, we investigate kinetic-theoretical schemes deriving the Boltzmann equation. We may derive the Boltzmann equation consistently by considering the Liouville equation to govern the distribution of a system in the phase space which is not symmetrical in the microscopic sense. On the other hand, we cannot derive the equation consistently on the assumption of symmetry of the distribution; the Boltzmann collision integral is not compatible with the symmetry assumption.

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